Effects of Humidity and Elevated Temperature on the Density and Thermal Conductivity of a Rigid Polyisocyanurate Foam Co-Blown with CCl_3F and CO_2

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ABSTRACT: Measurements of density and apparent thermal conductivity are presented for specimens cut from rigid polyisocyanurate (PIR) foam co-blown with trichlorofluoromethane (CCl_3F) and carbon dioxide (CO_2). Eight specimens, nominally 580 by 580 by 27 mm, were prepared from two boards (1.2 by 2.4 m by 50 mm) of foam laminated with permeable facers. Four specimens were placed in an ambient condition of 22°C and 40% relative humidity (RH). The other four specimens were each placed in one of the following environments: 1) 60°C and <10% RH; 2) 60°C and 40% RH; 3) 60°C and 60% RH; and 4) 60°C and 75% RH. Measurements of apparent thermal conductivity at 24°C were conducted over a period of 372 days at approximately 50-day intervals. Curves of specimen mass, volume, density, and thermal conductivity versus time are presented, and the implications of changes in these properties are discussed.

1. INTRODUCTION

RIGID POLYISOCYANURATE FOAM is a cellular plastic insulation that entraps a gaseous blowing agent(s) within microscopic cells of a polymer matrix. The cells of the foam are primarily closed, and because of the low thermal conductivity of the entrapped gas, the foam is an effective

insulator. Unfortunately, however, the cell walls are permeable. With time, the blowing agent(s) can escape from the cells while ambient gases such as N_2, O_2 and water vapor diffuse relatively quickly through the cell walls and permeate the foam [1,2]. The resulting change in the gas composition of the foam with time and the corresponding decrease in its insulating capability is commonly referred to as the "aging" of the foam.

For several years, manufacturers of rigid polyisocyanurate (PIR) foam have utilized trichlorofluoromethane (CCl_3F)[1] as a blowing agent for production of the foam. However, recent changes in the laws protecting stratospheric ozone (O_3), as well as an excise tax on the sale of chlorofluorocarbons (CFCs), have increased industry's incentive to curtail production of CFCs, including CCl_3F. Manufacturers of rigid polyisocyanurate foam have developed products with alternative blowing agents [3] or have reduced the amount of trichlorofluoromethane (CCl_3F) by adding a co-blowing agent. One technique used in the latter case is to increase the water content of the formulation by an appropriate amount to augment the production of gaseous carbon dioxide (CO_2) from the water-isocyanate reaction during foaming [4].

In previous publications [5,6], we have reported the effects of various environmental conditions on the microstructure, chemical, physical, and thermal conductivity properties of PIR foams blown with CCl_3F. In this paper, we present the effects of humidity at elevated temperature on the aging of a foam co-blown with CCl_3F and CO_2. The investigation was a combined effort by the Building Environment and Building Materials Division in the Building and Fire Research Laboratory at the National Institute of Standards and Technology. The objectives were: 1) to quantify the effect of elevated temperature and humidity on the aging of PIR foam; and 2) to attempt to correlate material degradation with measurements of apparent thermal conductivity[2]. This paper focuses primarily on the first objective and describes the preparation of specimens, conditioning environments, and measurements of specimen mass, volume, density, and thermal conductivity. Results are compared with data obtained previously from an aging study of rigid PIR foam blown only with CCl_3F [6]. The microstructure and chemical properties of both foams are discussed elsewhere [7].

2. SPECIMENS

Three boards of rigid PIR foam were taken consecutively from a product

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[1]Also known as Refrigerant-11. For the remaining text, all numeric references to refrigerants will be described by standard designations of refrigerants in accordance with ANSI/ASHRAE Standard 34–78. Specifically, the prefix R will be used to denote a refrigerant (e.g., R11 for Refrigerant-11).

[2]For brevity, the term thermal conductivity shall be used in the remaining text.

lot manufactured in December 1991. The boards were manufactured by a continuous "double-band laminate" process in which the formulation mixture was applied between two lamination facers. The foam was a polyurethane-modified polyisocyanurate made by mixing a polymeric diphenyl methane diisocyanate (PMDI) with a mixture of polyol, catalyst, and surfactant. The formulation decreased the amount of the physical blowing agent, CCl_3F, by increasing the water content in the formulation to produce CO_2 from the chemical reaction of water and isocyanate. The air-permeable facers were cellulosic material with reinforcing glass-fibers. The boards were delivered to NIST on 9 December 1991, and on 10 December 1991. Two of the boards were cut into eight equal-size sections (580 by 580 mm) and then passed several times through a belt-driven sander to remove
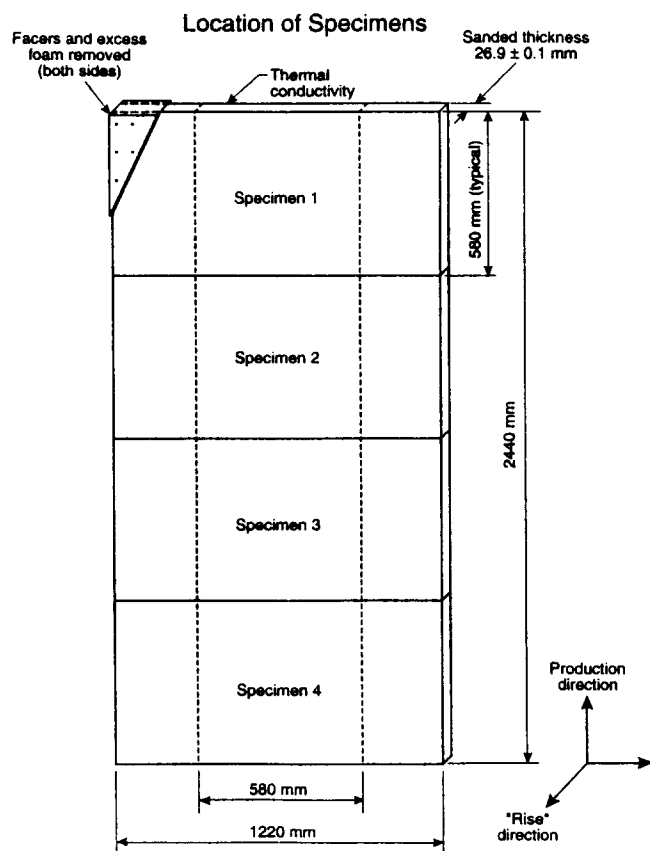

FIGURE 1. Sampling pattern of specimens of rigid PIR foam.

Table 1. Conditioning environments (air).

Environment	Specimen	Board	Temperature (°C)	Humidity (% RH)
1	1,2,3,4	1	22 ± 1	40 ± 2
2	5	2	60 ± 1	<10*
3	6	2	60 ± 1	40 ± 2
4	7	2	60 ± 1	60 ± 2
5	8	2	60 ± 1	75 ± 2

*Dry heat, humidity uncontrolled.

the facers and excess foam. Care was taken to remove equal portions of foam from both sides of the specimens. Figure 1 illustrates the sampling pattern of a single board. Specimens were selected from the center of the board parallel to the direction of production (Figure 1). The average thickness and maximum variation of each specimen were 26.9 ± 0.1 mm. The average was determined from 5 measurements per specimen ($n = 5$).

3. CONDITIONING ENVIRONMENTS

The conditioning environments are detailed in Table 1. Ambient air at 22°C and 40% RH was selected as a basis for comparison, and four replicates from one board were wrapped in a black polyethylene bag and placed in this environment. The other four specimens were each placed in air at the following conditions: 1) 60°C, <10% RH (humidity uncontrolled); 2) 60°C, 40% RH; 3) 60°C, 60% RH; and 4) 60°C, 75% RH. A temperature of 60°C was selected because of its historical popularity in several other aging studies [8-11].

4. EXPERIMENTAL

Initial measurements of specimen mass (m_i), volume (V_i) density (ϱ_i) and thermal conductivity (λ_i) were determined within five days after the specimens were sanded. Immediately after the initial measurements, the specimens were placed in their respective conditioning environments (Table 1). Subsequent measurements of m, V, ϱ, and λ were conducted at approximately 50-day intervals over a period of 372 days. Values of m, V, and ϱ were determined at 22°C; λ at 24°C. To minimize the effect of water on the measurements of thermal conductivity, specimens conditioned at 60°C and at 40%, 60%, and 75% RH were placed in an environment of 60°C, <10% RH (humidity uncontrolled) for 24 hours prior to measurement of λ.
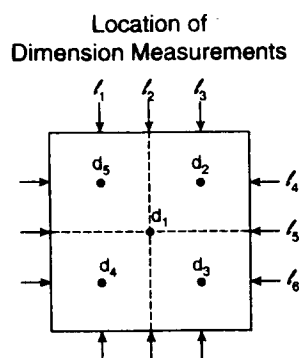
Location of
Dimension Measurements

FIGURE 2. Location of dimension measurements of specimens.

A. Mass (*m*), Volume (*V*), and Density (ϱ)

Material properties—m, V, and ϱ—of each specimen were determined at
ambient condition (22°C) prior to measurements of thermal conductivity.
The mass (m) was measured with a precision digital balance (0.1 g resolution)
and corrected for the buoyant force of air at ambient condition[3] (ϱ_{air} = 1.2
kg/m³ [12]). Linear dimensions (ℓ,d) were measured at the positions illus-
trated in Figure 2, averaged, and used to compute V. The specimen density
(ϱ) was determined from the relation $\varrho = m/V$. The uncertainty in ϱ was
generally estimated to be ±0.6%. For specimens conditioned at 60°C and
high humidity, the uncertainty in ϱ increased to as high as ±1.9% due to
warping of the specimen.

B. Thermal Conductivity (λ)

Measurements of thermal conductivity (λ) were conducted using a heat-
flow-meter (HFM) apparatus conforming to ASTM Test Method C 518. As
illustrated in Figure 3, the HFM apparatus utilized a single heat-flux-
transducer embedded at the center of the bottom plate. Measurements of
thermal conductivity were conducted at a mean specimen temperature (T_M)
of 24°C and a temperature difference (ΔT) of 22°C across the thickness of
the specimen. Heat flow through the specimen was parallel to foam rise
(Figure 1). Prior to each set of measurements, the HFM apparatus was cali-

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[3]The need to apply buoyancy corrections to mass measurements leads to adopting the terms
"apparent mass" and "apparent density." However, for brevity, all remaining text will simply use
the terms "mass" and "density."

brated using a Transfer Standard selected from an internal lot (Lot 1970) of Standard Reference Material of high-density fibrous-glass boards [13]. Calibration measurements were conducted at a T_M of 24°C and a ΔT of 22°C across the thickness of the specimen. The thickness and bulk density of the Transfer Standard were 26.2 mm and 139 kg/m^3, respectively. Estimates of uncertainty in the apparatus have been presented previously [14,15]. Repeatability of the apparatus for specimens of rigid PIR was better than 1% (3 times the standard deviation) [14]; overall uncertainty was $\pm 3.5\%$ [14]. The overall uncertainty was defined as the maximum deviation from the one-metre guarded hot plate [16] (ASTM Test Method C 177) for measurements of the same specimens [14].

5. RESULTS AND DISCUSSION

The changes in mass (m), volume (V), density (ϱ), and thermal conductivity (λ) of the rigid PIR foam are illustrated in Figures 4 through 7, respectively. The initial time (t_i) was taken to be when the specimens were sanded. In general, the results indicated that the changes in m, V, ϱ, and λ were more substantial for exposure at 60°C than for ambient conditions. Furthermore, the results indicated that at 60°C, the initial changes were greater at higher humidities. These results were consistent with our previous data [6], further supporting our contention that elevated temperature and humidity interact to produce greater changes in rigid PIR foam than either parameter alone.

A. Change in Mass with Time

At ambient conditions of 22°C and 40% RH, mass initially decreased slightly ($\approx 0.1\%$) after 30 days and subsequently increased to a maximum of about 1.3% after 250 days, as noted in Figure 4. Thereafter, the mass declined slowly to a value of about 1% after 372 days. At 60°C and $< 10\%$ RH, the specimen initially gained mass to a maximum of 0.4% after 83 days.
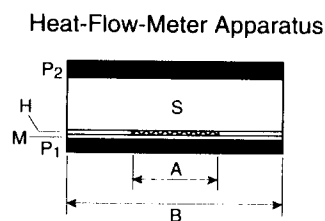
Heat-Flow-Meter Apparatus

FIGURE 3. Heat-flow-meter apparatus (ASTM Test Method C 518): $A = 254$ mm; $B = 610$ mm; H = heat-flux-transducer; M = acrylic plastic substrate; P = heating or cooling plate; S = specimen.
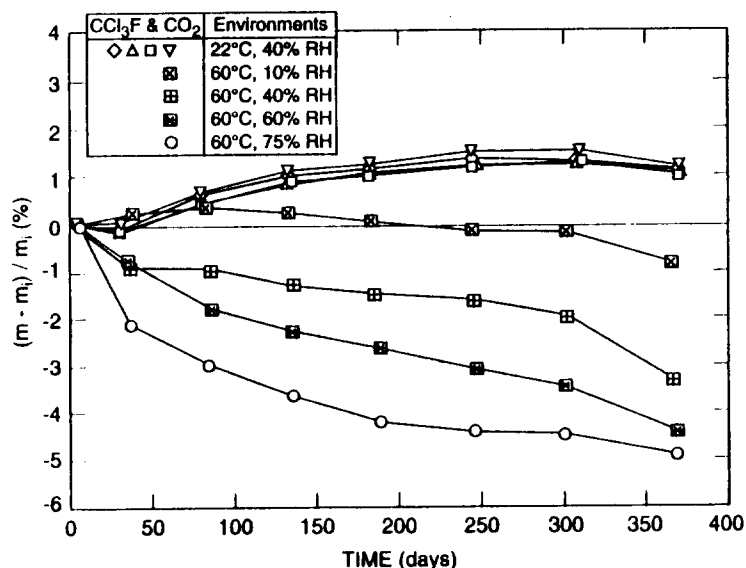
FIGURE 4. Percentage change of specimen mass (m) at 22°C for a rigid PIR foam aged at 22 C, 40% RH and 60 C at humidities of 10, 40, 60, and 75% RH.

Subsequently, the specimen gradually lost mass to a value of -0.8% after 372 days. At 60°C and humidities of 40, 60, and 75% RH, mass gradually decreased to values of -3.3, -4.4 and -4.9%, respectively, after 372 days. An explanation for these changes is presented below.

The net change in mass of a rigid PIR foam was the algebraic sum of the gains and losses resulting from several simultaneous processes. Previously, we postulated three processes that contributed to a gain in mass, and three that contributed to a loss [6]. For this study, we modified one process to include the loss of the blowing agent, CO_2. The processes contributing to a gain were 1) formation of reaction products from unreacted isocyanate with water during exposure; 2) diffusion of air and water vapor into the cell cavities; and 3) sorption of water in the cell-wall polymer (membranes and struts). The processes contributing to a loss were 4) unreacted materials evaporating from the polymer; 5) erosion of foam material; and 6) loss of blowing agents R11 and CO_2, either by diffusion or cell rupture. A complete analysis of each process is beyond the scope of this study, but a brief argument for the dominant processes follows.

The increase in mass due to 1) reactions of unreacted isocyanate (NCO) with water was believed small because the residual amount of NCO group in the foam was small, as shown previously by FTIR measurement [5]; the

gain was offset by the loss of gaseous products (CO_2) resulting from the NCO-H₂O reactions [17]. We interpreted the increase of mass to be due primarily to 2) diffusion of air (essentially N_2 and O_2) and water vapor into the foam and 3) sorption of water in the polymer. The loss due to 4) unreacted materials evaporating from the polymer was dismissed because of their small residual amount [5] and high temperature of evaporation ($\gg 60°C$). The process of 5) foam erosion must be accompanied by a reduction in volume and should have little effect on the density. In actuality, the specimens exposed at 60°C and different humidities increased in size (Figure 5) and the density decreased (Figure 6), suggesting that little erosion occurred. As a result, we interpreted the loss of mass to be due to 6) the loss of blowing agents CO_2 and R11. The loss of R11 from rigid PIR foam has been confirmed by Fourier transform infrared spectroscopy (FTIR) [6,7]. Thus, the dominant processes for the mass change of the foam were diffusion of low-density gases, N_2 and O_2, and water vapor into the foam, and higher-density gases, CO_2 and in particular, R11, from the foam.

The diffusion rate of R11 in rigid polyurethane foams is substantially lower than N_2, O_2 or CO_2. Brehm and Glicksman [18] have reported effective diffusion coefficients (D_{eff}) at 60°C of 12.3×10^{-8}, 88.8×10^{-8}, 351×10^{-8}, and 0.959×10^{-8} cm²/s for N_2, O_2, CO_2, and R11 in a rigid
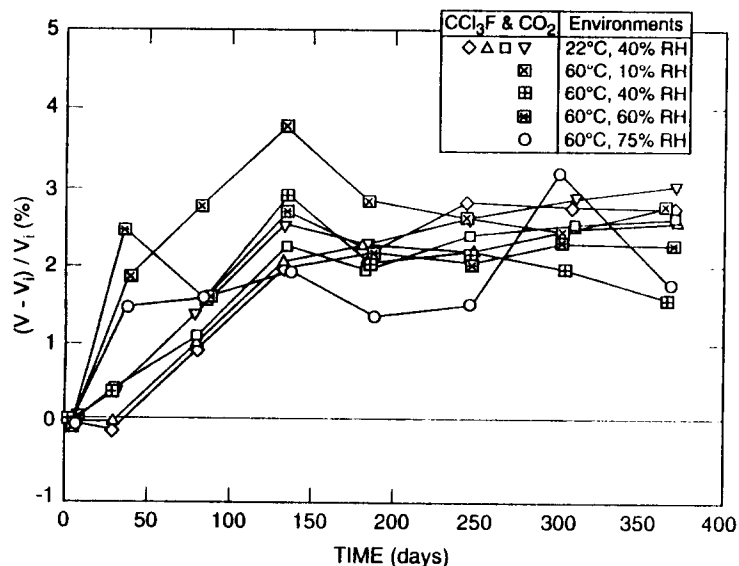

FIGURE 5. Percentage change of specimen volume (V) at 22°C for a rigid PIR foam aged at 22°C, 40% RH and 60°C at humidities of 10, 40, 60, and 75% RH.
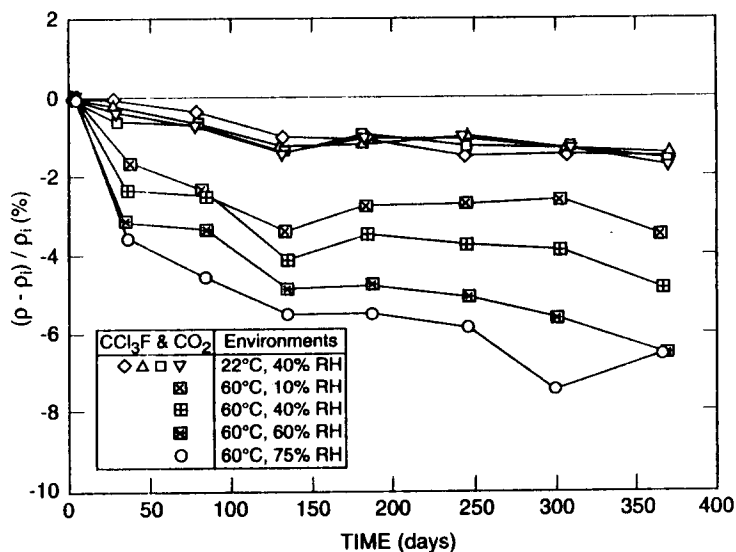
FIGURE 6. Percentage change of specimen density (ϱ) at 22°C for a rigid PIR foam aged at 22°C, 40% RH and 60°C at humidities of 10, 40, 60, and 75% RH.

polyurethane foam. In addition, environmental conditions such as moisture also affect the diffusion rate of R11. For example, using an FTIR technique, Nguyen et al. [7] determined values of D_{eff} at 60°C to be 10.1 × 10⁻⁸, 22.2 × 10⁻⁸ and 38.4 × 10⁻⁸ cm²/s for R11 in rigid PIR foam exposed to relative humidities of <10, 60, and 75%, respectively. Furthermore, the mass change of the foam is a function of the amount and density of the constituent gases within the cell cavities. The density of R11 is approximately three to five times greater than that of the other gases (5.8 kg/m³ for R11 versus 1.2, 1.3, and 1.8 kg/m³ for N_2, O_2, and CO_2, respectively,[4] at 25°C and 101.3 kPa). For a constant volume, equal exchanges of these gases in the cell cavities (N_2 and O_2 gain versus CO_2 and R11 loss) would result in a substantial mass loss for the foam.

The initial small loss of mass ($\approx 0.1\%$) observed in Figure 5 for specimens conditioned at 22°C and 40% RH was probably due to the rapid escape of CO_2 from the foam. The subsequent mass gain for these specimens was attributed to the intrusion of air and water vapor in the cell cavities, and sorption of water vapor in the polymer. Both processes probably contributed to

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[4]The densities of O_2, N_2, CO_2, and R11 were obtained from References [19] and [20], respectively.

net gain in mass ($\approx 1.3\%$), but the relative effects of these two processes were unknown. Note that the small initial gain in mass ($\approx 0.4\%$) for the specimen at 60°C and < 10% RH was most likely due to the diffusion of air into the foam. The gradual loss of mass with time was attributed to the escape of R11. At 60°C and high humidities, the loss was immediate and consistent with the higher value of D_{eff} of R11 (38.4×10^{-8} cm²/s) at 60°C, 75% RH reported by Nguyen et al. [7]. At laboratory ambient, the mass loss gradually dominated after about 300 days of exposure. An additional factor that may have affected the mass change was the presence of "well rounded" holes observed in the cell walls [6,7]. Although the mechanism for formation is unknown, their presence likely facilitated the escape of blowing agents (R11 and CO_2) from the specimens.

The effect of temperature on diffusion is well documented [18,21]. The effect of water probably accelerated the loss of R11 by affecting the polymer chain mobility and/or plasticizing the foam polymers. The presence of water molecules between the polar chains of the polyurethane-polyisocyanurate polymers increased their free volume. This enhanced the gas permeability of the polymer as well as its capability to sorb solvents. Kaplan and Tabor [22] have shown that humidity increased the oxygen permeability of thermoset polyurethane films having glass transitions near or below 25°C. The effects of water vapor on chain mobility in polymers with affinity for water have been documented [23].

B. Change in Volume with Time

The increase in volume was affected initially by temperature and humidity (Figure 5); however, after 372 days, the increase for all specimens was similar, from 1½ to 3%. At 22°C and 40% RH, volume gradually increased about 2½ to 3% over 372 days. For specimens at 60°C and different humidities, the initial rate of increase was relatively fast, but slowed after about 100 days. The specimens at 60°C and < 10, 40 and 60% RH obtained relative maxima at 135 days followed by a subsequent decrease in volume. At 60°C and 75% RH, the volume obtained a relative maximum (3.2%) at 300 days.

We hypothesized that the increase in volume of rigid PIR foam was primarily a result of R11 being sorbed by the polymer (swelling) and the presence of water vapor, a secondary factor [6]. Several studies [24–26] have investigated the solubility of R11 in polyurethane (PUR) and polyisocyanurate (PIR) foam. The solubility of R11 in the solid phase of rigid PUR foam has been measured previously by Steinle [24] using gas chromatography. His results indicated that after 6 months, 50 to 60% (by weight) of the R11 content was soluble in the solid phase of the foam. Using a similar analysis, Brandreth and Ingersoll [25] found that 8 to 63% of the total R11 was in the

polymer for eleven different types of rigid PUR foam. More recently, Gaarenstroom et al. [26] studied the distribution of R11 in aged production specimens of PUR and PIR foams using gas chromatographic analysis with flame ionization. Their study indicated that for the PIR foam (13 years old), about half of R11 was in the polymer phase and about half was in the gas phase. Moreover, their study concluded that R11 does not "appreciably decompose in either type of foam, nor does it react with the polymer" [26].

In theory, swelling occurs in a polymer when the solvent (the adsorbate) has sufficient affinity for the polymer (the adsorbent) to form intimate "solid solutions" (i.e., adsorbate molecules held between the adsorbent side chains) with the polymer. Swelling is maximized when the adsorbate and the adsorbent have similar solubility parameters. When an adsorbate is held only on pre-existing surfaces of a powder or rigid pores of solid, very little swelling accompanies adsorption. Because the solubility parameters of R11 and a polyurethane polymer are closer to each other than water and a polyurethane polymer, it is expected that polyurethane polymers sorbed more R11 than water. Figure 5 shows that in the presence of very little moisture (60°C and < 10% RH), the foam swelled (3.8%) during exposure. Since the only adsorbate in the foam was R11 and there was also a gradual loss in mass as a function of time (Figure 4), the swelling at 60°C and < 10% RH was interpreted primarily to be due to the formation of solid solution in the cell walls of the PIR foam by R11 solvent.

Another contributing factor for the increase in volume may have been "creep" in the polymer—that is, slow, permanent deformations at and above the glass transition temperature (T_g) of the polymer, which can be significant when a long-term load is applied to the foam [27]. In this case, a positive pressure gradient between the cell-gas pressure and atmospheric pressure can cause expansion of the foam, particularly at elevated temperatures [28]. In this study, neither the T_g of the polymer nor the cell-gas pressure of the foam were determined, and the relative effect of creep was unknown. The presence of water, however, would also lower the glass transition temperature of the polymer [23], enhancing the potential for creep occurring within the polymer. The subsequent contraction of volume for some specimens after 135 days (Figure 5) was believed due, in part, to desorption of R11 from the polymer. However, the presence of holes in cell walls, as noted above, most likely alleviated any positive pressure gradients between the cells and atmospheric pressure and would also probably result in contraction of the foam. This phenomenon is similar to that observed when cells rupture during exposure to elevated temperature [28]. Other factors, including thermal expansion of the polymer and cell rupture, were dismissed after supplemental measurements were conducted [6,7].

An increase in the temperature of the foam will increase the pressure of the

gases in the cells (about 13% from 22°C to 60°C), increasing not only the pressure gradient between interior and ambient (expansion) but also the solvation of the polymer by the R11 solvent (swelling). As mentioned above, the processes of sorption and diffusion of R11 into the polymer are temperature dependent, which may, in part, explain the difference in initial rates of swelling at 60°C and 22°C (Figure 5). The corresponding increase in the pressure gradient between the interior and ambient should accelerate the rate of permeation of R11 into the cell walls since the rate of permeation is directly proportional to the pressure difference across the wall. An increase in temperature also increases the free volume of the polymer, which subsequently increases the sorption of the R11 solvent. The presence of sorbed water in the polymer would tend to "plasticize" (i.e., soften) the cell walls, accelerating the sorption and diffusion of R11 into the cell walls. In our previous study [6], the effect of humidity at 60°C increased the volume of a rigid PIR foam between 5 and 6%. However, in this study, the effect was 4% at most (Figure 5). This difference may be attributed to a reduced level of R11 in the foam. In theory, a lower amount of R11 would result in less swelling.

C. Change in Density with Time

Specimen density (ϱ) is dependent on specimen mass (m) and volume (V), as defined by the relation $\varrho = m/V$. The change in ϱ (Figure 6) was similar to the change in specimen mass (Figure 4), except for specimens aged at laboratory ambient (22°C, 40% RH). For these specimens, ϱ decreased about 2% due to swelling of about 3% (Figure 5) and a mass gain of about 1% (Figure 4). At 60°C, density decreased by 3.5, 4.8, 6.5, and 6.6% for humidities of <10, 40, 60, 75% RH, respectively.

D. Change in Thermal Conductivity with Time

The thermal conductivity (λ determined at 24°C) increased over time and was affected by temperature and humidity (Figure 7). Initially, the increase for specimens conditioned at 60°C was greater than for specimens conditioned at 22°C and 40% RH. These data are consistent with our previous results [6] and other experimental studies [7–10, 29–32] that have shown elevated temperature to increase the thermal conductivity of rigid PIR/PUR foam. However, after 372 days, the increase in λ for all specimens was similar, from 34 to 44%. In our previous study [6], the effect of humidity at 60°C increased λ by 49 to 74% after 357 days. Here, the effect of humidity was not as pronounced, but seems more of a factor after 200 days. At 60°C and humidities of <10, 40, 60, and 75% RH, λ at 24°C increased by 35, 35, 38, and 44%, respectively, after 372 days. The differences will be discussed in the following pages.
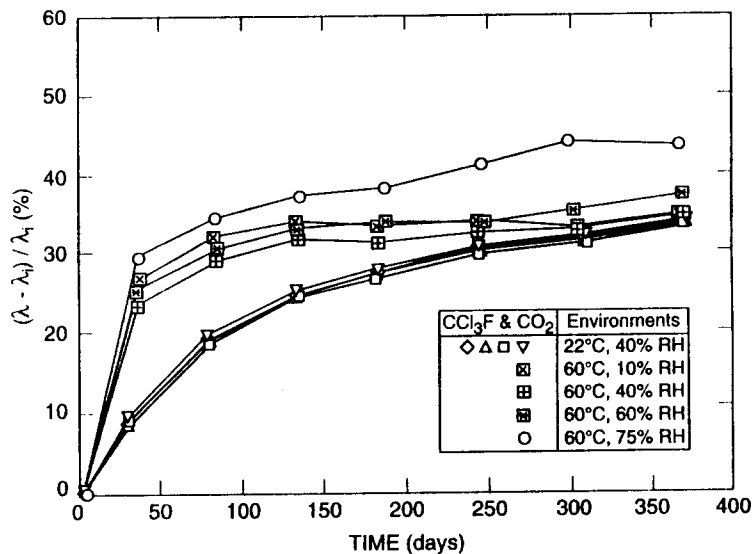
FIGURE 7. Percentage change of specimen thermal conductivity (λ) at 24°C for a rigid PIR foam aged at 22°C, 40% RH and 60°C at humidities of 10, 40, 60 and 75% RH. Lambda measured parallel to foam rise.

The thermal conductivity (λ) of a foam can be expressed as the sum of three individual contributions [33]:

$$\lambda = \lambda_g + \lambda_s + \lambda_r$$

where λ_g is the thermal conductivity of the gas mixture in the cells, λ_s is the thermal conductivity of the polymer (cell membranes and struts), and λ_r is the radiative component of thermal conductivity. Convective heat transfer is negligible for the small cells (generally less than 2 mm in diameter) of present production foams [34]. The contributions of λ_g, λ_s, and λ_r have been estimated by Cunningham and Sparrow [35] to be 44, 23, and 33%, respectively, for a free-rise laminate of PUR foam (30 kg/m^3) blown with R11. Since the thermal conductivity of CO_2 is greater than R11, one might expect a higher λ_g and a corresponding higher λ for a rigid PIR foam co-blown with CO_2 and R11, assuming all other factors equal (e.g., cell size, polymer formulation, age of foam, etc.).

As was the case with the change in specimen mass, the change in λ of a rigid PIR/PUR foam was primarily the result of diffusion processes changing the gas mixture within the cells, in this case increasing λ_g. With time, am-

bient gases (N_2, O_2, and water vapor) with a relatively high thermal conductivity diffused into the cells, while R11 departed by both sorption into the polymer and diffusion through the cell wall. In this study, the departure of CO_2 occurred primarily in the first 30 days (Section 5A), but not enough data was taken to see an effect on the thermal conductivity (Figure 7). The net effect was that the thermal conductivity of the cell-gas mixture (λ_g) increased, thereby increasing λ. As will be discussed below, aging in humid environments also appeared to affect one or both of the other mechanisms of heat transfer (λ_s, λ_r), but to a lesser extent.

E. Change in Foam Additive with Humidity

While examining the microstructure of the foam, an extremely interesting phenomenon was observed and is noted here because it may affect the above properties. We observed particles of potassium chloride (KCl) on the surfaces of the cell membranes and struts. These particles are displayed in the micrographs of Figure 8 for specimens of foam exposed for one year in environments of 60°C and relative humidities of 40 and 75%. As seen in the micrographs, the size of the particles appeared to increase as a function of humidity [6]. The origin of the particles of KCl is unknown, but it is possible that the particles were derived from a reaction of a potassium-based catalyst used in the formulation and hydrolyzed chlorine in the PMDI (polymeric diphenyl methane diisocyanate). Since KCl is an ionic, hygroscopic, and corrosive material, its presence could have other implications, such as increasing the foam's water uptake or thermal conductivity.

F. Comparison with Rigid PIR Foam blown only with CCl₃F

In previous paper [6], we examined the macroscopic thermal and material properties of another commercial product of rigid PIR foam blown primarily with R11. The foam boards were manufactured during the last quarter of 1990 and delivered to NIST on 22 January 1991. After delivery, the boards were stored in an environment of 22 ± 2°C, 40 ± 10% RH for three months. As in this study, eight specimens, nominally 600 by 600 mm, were then cut and aged in air for a period of 357 days in the same environments described in Table 1. Measurements of specimen mass (m), volume (V), density (ϱ), and thermal conductivity (λ) were determined at intervals of about 50 days. An interesting correlation for the thermal conductivity (λ) data at 24°C as a function of its corresponding specimen density (ϱ) was found, and these data are included again in Figure 9 for comparison.

Figure 9 shows thermal conductivity (λ) at 24°C as a function of specimen density (ϱ) at 22°C for data from our present and past studies. The data for rigid PIR foam co-blown with R11 and CO_2 are shown as open symbols; data for the R11 foam are shown as solid symbols. Remember that within
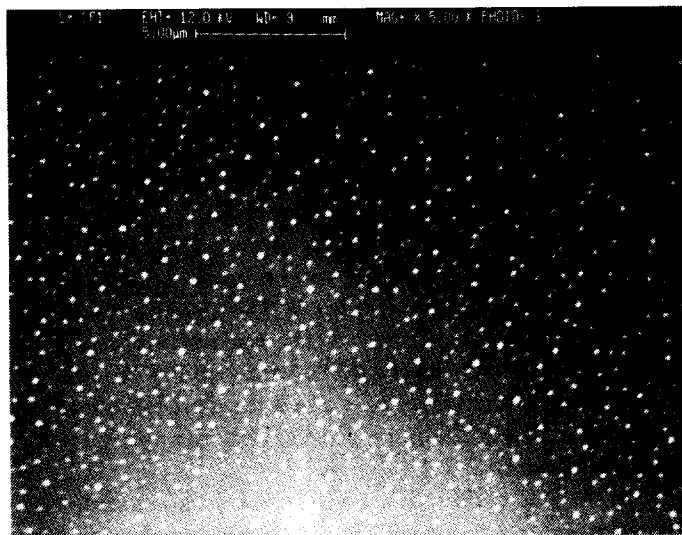
FIGURE 8a. Particles of potassium chloride on cell membrane of rigid PIR foam exposed to 60°C, 40% RH for one year (magnification 5000x).
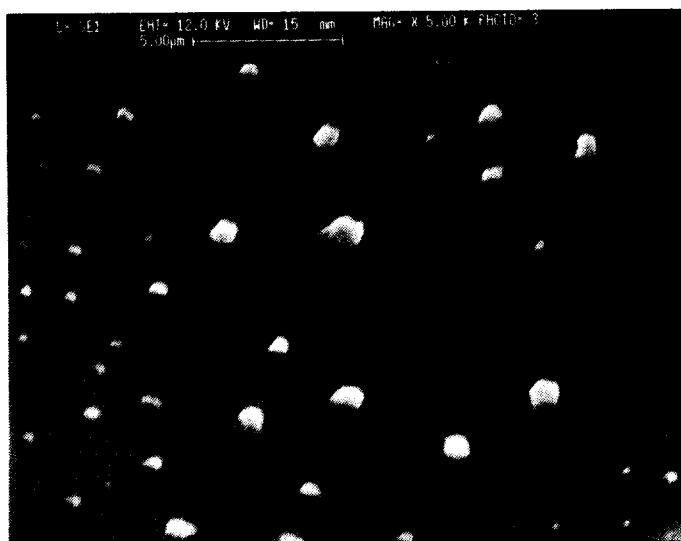

FIGURE 8b. Particles for potassium chloride on cell membrane of rigid PIR foam exposed to 60°C, 75% RH for one year (magnification 5000x). Note increase in particle size.

each set of data, each specimen was exposed to the environments in Table 1 for one year. Also note that the time-histories for each foam are offset; that is, the specimens of each type of foam were prepared (sanded) at different times in their respective aging. Plotting λ as a function of ϱ results in a "composite" ϱ/λ curve for each set of data relegating the thermal conductivity-time (λ/t) dependency to the background. In other words, aging for a particular specimen in Figure 9 progresses from right to left; each subsequent data point for that specimen was determined at an interval about 50 days later. The initial values (i.e., $t_i = 0$ when the specimens were sanded) of ϱ and λ for each set of data are indicated in Figure 9. The average values of ϱ_i were 24.5 kg/m³ (R11/CO₂) and 26.9 kg/m³ (R11), respectively, and the average values of λ_i were 0.019 W/(m · K) (R11/CO₂) and 0.017 W/(m · K) (R11), respectively. The higher initial values of ϱ and λ for the co-blown foam could be due to several factors, including cell-size, polymer formulation, age of foam, or reduced amount of R11.

The change in thermal conductivity with density varied with exposure to the different environments (Figure 9). For specimens aged at laboratory ambient of 22°C and 40% RH, λ initially increased with a very small change in density, i.e., the data points show a vertical or almost-vertical rise. At
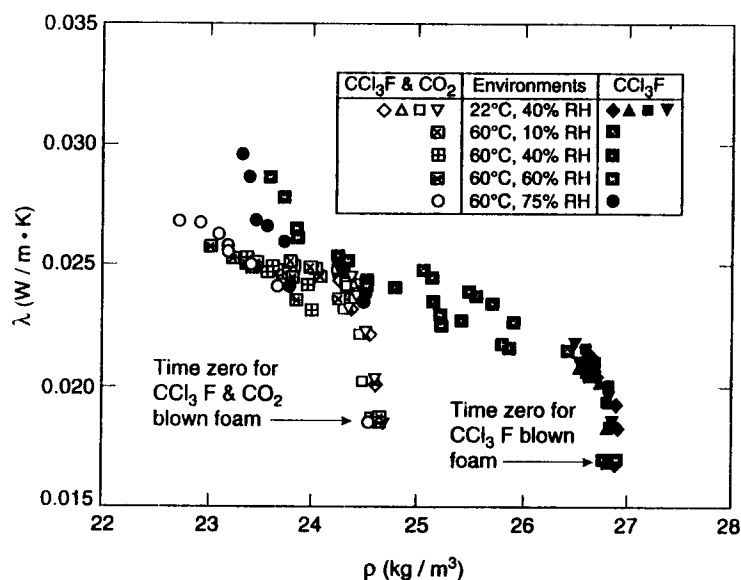

FIGURE 9. Thermal conductivity (λ) at 24°C as a function of density (ϱ) for rigid PIR foam. Lambda measured parallel to foam rise. Specimens aged for one year.
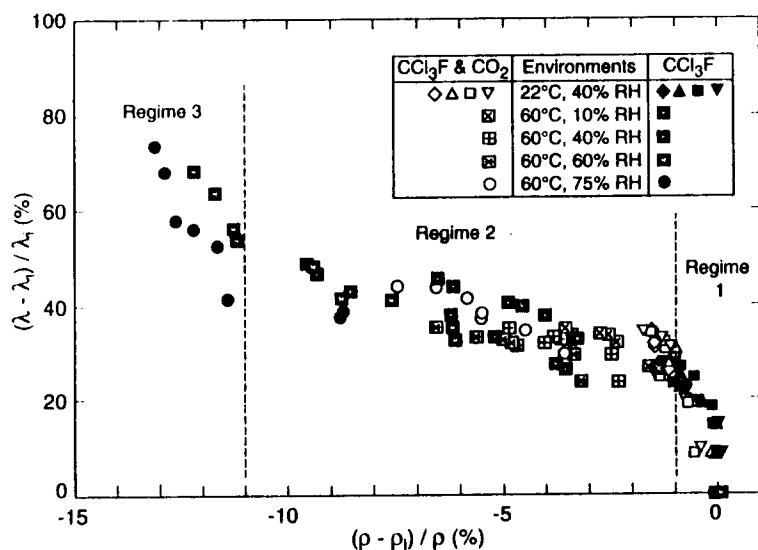
FIGURE 10. Percentage change in thermal conductivity as a function of percentage change in density for rigid PIR foam. Lambda at 24°C measured parallel to foam rise. Specimens aged for one year.

60°C and different humidities, λ and ϱ were negatively correlated — in other words, λ increased as ϱ decreased. As mentioned above, we attributed the decrease in ϱ primarily to the loss of R11 from the foam. Accordingly, the density of the co-blown foam, which was blown with a reduced amount of R11, decreased less than the foam blown with only R11. Interestingly, although λ, of the co-blown foam was higher, the change in λ was not as great as the foam blown only with R11. It is significant to note that for aging at 60°C and high humidities of 60 to 75% RH, the value of λ for both foams approached or exceeded the upper limit of the range of "stabilized k-factor" published by SPI[5] [36] and ASHRAE[5] [37]. The range of typical "stabilized k-factors" of R11-blown PUR/PIR foams with permeable or no facers has been reported to be 0.023 to 0.026 W/(m · K) [36,37].

Another comparison of the data for rigid PIR co-blown with R11 and CO_2 and rigid PIR foam blown with R11 is illustrated in Figure 10. This figure presents the percentage change in thermal conductivity $(\Delta\lambda = (\lambda - \lambda_i)/\lambda_i \cdot 100)$ at 24°C as a function of the percentage change in specimen density $(\Delta\varrho = (\varrho - \varrho_i)/\varrho_i \cdot 100)$. Here, by plotting $\Delta\lambda$ as a func-

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[5]The Society of the Plastics Industry, Inc. and the American Society of Heating, Refrigerating and Air Conditioning Engineers, Inc., respectively.

tion of $\Delta\varrho$, the data are overlaid and the similarity in aging of the two lots of foam is clearly revealed. Referring to Figure 10, the aging of the foam is characterized by three regimes. Initially, $\Delta\lambda$ increased about 15% with no change in ϱ, i.e., the plot of $\Delta\lambda$ increased vertically. In this regime (1), air diffused into the foam, but the R11 was, for the most part, captive. During this time-period, some of the R11 left the cell-cavities by sorption and diffusion into the polymer. This is consistent with the swelling noted in these specimens (see Section 5B). In regime (2), the increase in $\Delta\lambda$ from 15 to about 50% was accompanied by a decrease in $\Delta\varrho$ of about 10%. During this time-period, R11 was leaving the foam (i.e., increasing λ with decreasing ϱ) and intrusion of air (and water vapor) continued. Above 50%, $\Delta\lambda$ increased with smaller decreases in $\Delta\varrho$ (i.e., in a curvilinear fashion), indicating a regime (3) where the amount of R11 was depleted or at low concentrations in the cells, and the intrusion of air (and water vapor) continued to increase λ_g.

Also in Figure 10, some systematic trends are noted in the data. In general, except for the extreme range of $\Delta\varrho$ ($\Delta\varrho < -1\%$ and $\Delta\varrho > -13\%$), the change in λ was linearly correlated with the change in ϱ within a tolerance of about $\pm 5\%$. In other words, for $\Delta\varrho$ between -1 and -13%, $\Delta\lambda$ varied by about $\pm 5\%$. This suggests that the presence of R11 solvent and/or water vapor in the cell walls may affect the rates of diffusion of the cell gases (R11, O_2, and N_2). So for a given $\Delta\varrho$, the cell-gas composition may not be the same for all exposures, and the aging of the foam could be described by a family of curves dependant on environmental exposure. More data is required for verification. The systematic differences may also be due to changes in one or both of the other components of thermal conductivity (λ_s, λ_r). In theory, R11 solvent or water sorption in the cell walls could change the thermal conductivity of the polymer, the radiative properties of the polymer, or both.

6. SUMMARY AND CONCLUSIONS

This study examined the macroscopic thermal and material properties of a rigid PIR foam ($\varrho_i = 24.5$ kg/m^3) co-blown with CCl_3F and CO_2. Specimens, nominally 580 by 580 mm, were cut from a commercial product and aged in air for a period of 372 days. The effect of five environments on aging was studied. These included ambient conditions of 22°C and 40% RH and 60°C at <10, 40, 60, or 75% RH. During the test period, measurements of specimen mass (m), volume (V), density (ϱ), and thermal conductivity (λ) were determined at ambient conditions at intervals of about 50 days. Measurements of thermal conductivity were determined at 24°C using a heat-flow-meter apparatus (ASTM C 518).

Over one year, the aging of rigid PIR foam co-blown with CCl_3F and

CO_2 affected the thermal conductivity (λ), as well as the specimen mass (m), volume (V), and density (ϱ). The combined factors of elevated temperature and humidity were shown to accelerate the aging of rigid PIR foam more than either parameter alone. Data from this study were compared to our previous one-year aging study of a rigid PIR foam blown with CCl_3F by means of a plot of density and thermal conductivity, and a plot of their relative percentage changes ($\Delta\varrho/\Delta\lambda$). Results indicated that the aging of a rigid PIR foam co-blown with CCl_3F and CO_2 was similar to a rigid PIR foam blown only with CCl_3F. Changes in the macroscopic properties — m, V, ϱ, and λ — were interpreted primarily as the result of air and water vapor penetrating into the foam, and refrigerant CCl_3F sorbing and diffusing through the polymer, and eventually departing (under conditions of high humidity at 60°C) from the foam. An examination of the foam's microstructure by scanning electron microscopy revealed particles of potassium chloride (KCl) on the cell membranes and struts. The origin and effects of the particles of potassium chloride are unknown.

7. ACKNOWLEDGEMENTS

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